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Correlation of Ionization and Structure

Chemical Engineering

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CORRELATION OF IONIZATION AND STRUCTURE

BY

JOSE ORIOL CARRERO

THESIS

FOR THE

DEGREE OF BACHELOR OF SCIENCE

IN

CHEMICAL ENGINEERING

COLLEGE OF SCIENCE

UNIVERSITY OF ILLINOIS

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May 31, 1912

THIS IS TO CERTIFY THAT THE THESIS PREPARED UNDER MY SUPERVISION BY

JOSE ORIOL CARRERO

ENTITLED Correlation of Ionization and Structure.

IS APPROVED BY ME AS FULFILLING THIS PART OF THE REQUIREMENTS FOR THE

DEGREE OF BACHELOR OF SCIENCE in

Chemical Engineering

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219478

CORRELATION OF IONIZATION AND STRUCTURE.

Introduction - Recent problems in the field of organic chemistry have caused the search for new methods for the determination of the chemical structure of organic compounds. The tendency is towards physico-chemical methods, different chemists using different physical constants. As an example Ostwald (1) and later Wegscheider (2) have employed the ionization constants of organic electrolytes.

Other constants such as the specific rotation of optically active compounds, magnetic rotation, molecular refraction, etc. have been successfully employed in certain cases.

A comparison between these physical methods for the determination of structure and the chemical ones is not out of place. In the chemical methods fairly large amounts of the substance are required for analysis. This requisite proves to be a handicap in most instances, for very often the yield of the substance under investigation is very poor. Again these chemical methods destroy the substance completely so that recovery is usually impossible.

On the other hand physico-chemical measurements present several decided advantages. Very small amounts of the substances are necessary. The substance is not destroyed so that recovery can be accomplished in case the materials are of a very valuable nature. The one drawback to this method is the high degree of purity needed in most cases in order to insure accurate results.

It is the purpose of this investigation to prove that there exists a relation between the ionization constants of halogen paraffin acids and their structures.

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Historical - Ostwald (1) was the first to recognize that there exists a definite relation between halogenated paraffin acids and their structures. It is his theory that the ionization constant of any acid is influenced by the substitution of a hydrogen atom by a halogen. For example this influence, called a factor, for a halogen in the (alpha) position is defined as the ratio $\frac{k}{k_o} = \frac{k\text{ (substituted acid)}}{k_o\text{(unsubstituted acid)}} = a$. This factor depends upon the nature and position of the halogen. For the , α, β, γ, positions it is called a, b, c, etc.

The factors a, b, c, etc. Ostwald (1) calls the influence of the substituted halogen. This is apparently an error, for the ionization constant of an acid depends upon the influence of the different atoms present in one molecule of the substance. According to this the factors a, b, c, etc. would not represent the influence of the substsuted halogen alone, but the influence of the substituted halogen and those of the other atoms present in one molecule of the substituted acid divided by the influence of the atoms in the unsubstituted acid.

Using his theory the following results are obtained for the factors for iodine in iodo-acetic and β-iodo propionic acids. The data used is corrected so that it is expressed in international ohms and the values chosen for Λ_∞(Na)(51.2) and Λ_∞(H)(350) at 25° are those given by A. A. Noyes (3) and K. E. Falk (3) from a summary of existing data. Iodo-acetic was measured by Walden (4) who gave the value 7.5×10^{-4} which corrected is 6.94×10^{-4}. β-iodopropionic acid was measured by Ostwald (1) who gave the value 9.0×10^{-5} which corrected is 84.26×10^{-6}. The values for the corresponding unsubstituted acids are chosen as 1.75×10^{-5} and 1.29×10^{-5} from corrected data of Ostwald (1) for acetic and propionic acids respectively. Hence

$$\frac{K \text{ (Iodo-acetic)}}{K_o \text{(Acetic)}} = 3.966 \quad = a \text{ for I in } \alpha\text{-position.}$$

$$\frac{k \text{ (}\beta\text{-Iodopropionic)}}{k_o \text{(Propionic)}} = 6.976 \quad = b \text{ for I in } \beta\text{-position.}$$

Theoretical - Recently further work and study has been carried on by Derick (5) on the influence of the substituted halogen on the ionization constants of different aliphatic acids. It is his theory that every atom in a molecule of the substituted or unsubstsiuted compound has its influence on the ionization constant of that compound. Having established this fact, the place influence of the substituted halogen is derived as follows:

Let K = Ionization constant of substituted acid.

K_o = " " " unsubstituted " .

$I\alpha, Cl$ = Influence of Cl atom in α position on K.

$I(CH_2ClCO_2H)$ = Influence of all atoms in one molecule CH_2ClCO_2H on K.

$I(CH_3CO_2H)$ = Influence of all atoms in one molecule CH_3CO_2H on K_o.

Now $I(CH_2ClCO_2H) = a\frac{1}{\log K}$ where a = a constant.

Also $I(CH_3CO_2H) = a\frac{1}{\log K_o}$ where a is same constant as in first equation

Then $I(CH_2ClCO_2H) : I(CH_3CO_2H) = \frac{\log K}{\log K_o}$. But the ratio $\frac{\log K}{\log K_o}$ Derick (5) finds numerically equal to 1.6830. The meaning of this ratio is that the influence of all the atoms in acetic acid is equal to one while that of all the atoms in chlor-acetic acid is 1.6830. If we examine the formula of chlor-acetic acid we note that neglecting chlorine, the remaining atoms differ from acetic acid by one H. atom. Hence 1.6830 - 1 = 0.6830 represents the difference between the influences of a chlorine and a hydrogen upon K. This is called the chlorine influence ($I\alpha, Cl$) for the alpha position. This assumes that the factor 1.6830 is made up additively of the influences of each atom in the molecule of the

acid.

Applying Derick's (5) rule to iodo-acetic and β-iodopropionic acids measured by Walden (4) and Ostwald (1) respectively, using corrected values for the ionization constants, we have

For iodo-acetic $\frac{\log K}{\log K_o} - 1 = 0.5060$

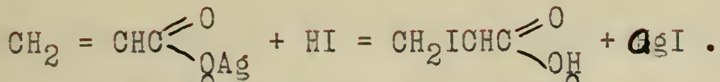
For β-Iodo propionic acid $\frac{\log K}{\log K_o} - 1 = .200.$

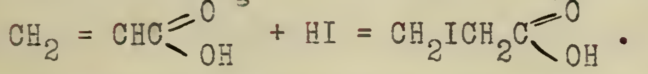
We find $I(\alpha, I) = 0.506$ and $I(\beta, I) = .200$

Derick (5) has further pointed that for chlorine, bromine, hydroxy, etc. radicals that $I\alpha : I\beta : I\gamma$ etc. $= \frac{I\alpha}{3} : \frac{I\alpha}{9} : \frac{I\alpha}{27}$ etc. This has been called the rule of thirds. From the above measurements it is evident that this rule does not apply to iodine. It is the purpose of this paper to test out this rule after obtaining more accurate data through the above.

Experimental—Preparation of β Iodo-propionic Acid – In this investigation two methods were used for the preparation of the acid.

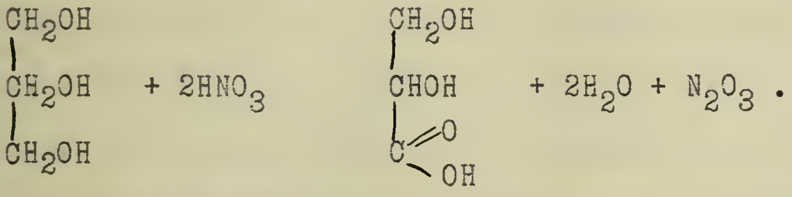
1 – In the first attempt I started with acrolein. The sample obtained was a very old one so that it was of a syrupy consistency. This was placed in a flask , mixed with a little water, and treated with silver oxide. The acrolein should be oxidized to acrylic acid according to the equation $CH_2 = CHC\begin{smallmatrix} {=}O \\ {\diagdown}H \end{smallmatrix} + Ag_2O = CH_2 = CHC\begin{smallmatrix} {=}O \\ {\diagdown}OAg \end{smallmatrix} + Ag.$ The reaction was carried on in a 100 cc round bottom Jena flask with a condenser. The reaction did not start until a little heat had been applied. Then a large amount of heat was evolved while the sides of the flask were covered with a silvery film. No attempt was made to separate the silver acrylate thus formed, for the quantity was small, but to the solution was added hydriodic acid. We should in this manner get two reactions to proceed simultaneously :

(1) 
$CH_2 = CHC\genfrac{}{}{0pt}{}{\nearrow O}{\searrow OAg} + HI = CH_2ICHC\genfrac{}{}{0pt}{}{\nearrow O}{\searrow OH} + AgI$.

(2) 
$CH_2 = CHC\genfrac{}{}{0pt}{}{\nearrow O}{\searrow OH} + HI = CH_2ICH_2C\genfrac{}{}{0pt}{}{\nearrow O}{\searrow OH}$.

I succeeded in obtaining a small amount of a precipitate which proved to silver iodide but on evaporation of the solution I could not obtain any β-iodo acid. The acid if formed at all was probably hydrolyzed and lost during the evaporation of the water.

2 - In the second attempt the method of Levy's (6) was used. This time I started with glycerine, which was diluted volume for volume by water. This on treating with fuming nitric acid yields glyceric acid.


$$\begin{matrix}CH_2OH\\ |\\ CH_2OH\\ |\\ CH_2OH\end{matrix} + 2HNO_3 \quad \begin{matrix}CH_2OH\\ |\\ CHOH\\ |\\ C\genfrac{}{}{0pt}{}{\nearrow O}{\searrow OH}\end{matrix} + 2H_2O + N_2O_3 \,.$$

I don't think the reaction goes on as easily as this because I found that some oxalic acid was formed at the same time. The reaction was carried as follows: 50 gms. of glycerine were placed in a 500 cc round bottom Jena flask. To this I added an equal volume of water, and shook the two until they were well mixed. Then 50 gms. fuming nitric acid were introduced at the bottom of the flask so that two distinct layers were formed. These layers were then allowed to mix slowly. Four samples were treated at the same time. Meanwhile the flask was kept in an ice bath for at least 11/2 days. This is essential as the two layers may mix slightly on the slightest jar and then a very violent reaction will occur. After standing from four to six days the reaction is complete. The mixture of glyceric acid, unchanged glycerine, nitric and probably some oxalic acid was diluted to twice its volume and placed in a dish on the water bath. This drove off the HNO_3 and N_2O_3 fumes. It was taken up with water when the residue had become of a

syrupy consistency. This was neutralized with lead carbonate. The lead salt thus formed was soluble in water so that evaporation was required before the salt crystallized out on cooling. I noticed during the evaporation that the solution would turn brown. On examination the color proved to be due to lead oxide precipitaying out, the solution becoming acid at the same time. This was prevented by having a slight excess of lead carbonate in the solution during the evaporation, which was filtered off just before crystallization took place. The salt was then dissolved in water. Here a difficulty was experienced in that only a portion about 3/4 to 4/5 of the salt would go into solution. The rest was almost insoluble in even hot water. The insoluble portion was filtered off and the soluble part titrated exactly with dilute sulphuric acid. (1-3). This precipitates lead sulphate and liberates free glyceric acid.

The solution of glyceric acid was filtered from the lead sulphate and concentrated. On concentration it was noticed that some solid crystalline substance would separate out. On analysis these crystals proved to be oxalic acid. To separate glyceric acid from oxalic acid I allowed the solution to cool when a fairly large amount of oxalic acid came down. It was filtered off and the glyceric acid was further concentrated. This treatment was repeated twice when no more oxalic acid separated out. The glyceric acid was then concentrated to a Sp. Gr. 1.26.

The insoluble portion of the lead salt was suspended in water and treated with sulphuric acid until the solution was slightly acid. The lead sulphate was filtered off. Then the solution was concentrated on the water bath. On cooling and standing a mass of crystals came

down. On examination they proved to be oxalic acid.

Preparation of β -iodopropionic acid -

1 - In the first trial I used a mixture of red phosphorous, iodine, and 3 cc. of glyceric acid. On warming slightly there was a vigorous almost violent reaction. Vapors of hydriodic acid and iodine issued from the mouth of the flask. The flask was cooled in ice water until the reaction slowed down. A very dark mass remained. This was extracted with carbon bisulphide. On evaporation it left a slightly brown product which on further purification yielded a bright yellow product. A subsequent analysis proved it to be iodoform.

2 - Second trial - 13 cc. of the glyceric acid are placed in a flask, 50 gms. phosphorous diiodide are added. There is very little reaction at first, but on warming slightly the contents of the flask boiled, and clouds of hydriodic acid escaped from the mouth of the flask. The contents of the flask are apt to become dark brown at this stage, but if the 13 cc. of glyceric acid are diluted with 10 cc. of water and then treated with phosphorous diiodide the solution does not darken so easily. There is one objection to this method. It makes the solution more dilute so that evaporation is required to obtain the product formed, and some of the iodo acid decomposes during this evaporation. When the reaction is complete some of the solution is evaporated off. On cooling the concentrated solution it solidifies, a thich mass of thin tablets of the acid being formed. Some of these were filtered on a Hirsch funnel, washed with a little water and dried between two clay plates. This product melted at 81 - 82°. The pure acid melts at 82°. The rest of the glyceric acid was treated in the same manner until a yield of 82 grams of the iodo acid had been obtained.

Ether and carbon bisulphide dissolve this acid readily, but as these solvents dissolve a good deal of the impurities present the acid cannot be obtained very pure from them. Instead I used ligroin, boiling point 60 - 82°. This solvent dissolves the acid readily when hot. On cooling the acid crystallizes out in beautiful white tablets which were filtered off and washed with cold ligroin. This process was repeated twice until a white product free from iodine was obtained. A series of melting points on the substance gave results as follows: 81.95°, 82.04°, 82.05°. The readings of the thermometer are corrected.

The product was placed in vacuo over calcium chloride in order to remove any ligroin it might contain. When this was accomplished the acid was tested qualitatively and quantitatively for iodine. The quantitative one gave result as follows:

Sample taken	Wt. AgI formed	Theoretical AgI	Diff.	% Diff.
0.1847	0.2174	0.2169	.0005	0.23%
0.1807	0.2126	0.2121	.0005	0.25%

Preparation of Sodium Salt of Iodo-acid -

Method I - The best method used for the preparation of sodium salts of organic acids is to prepare a concentrated solution of sodium hydroxide in absolute alcohol. This solution is then titrated with the solid acid using phenolphthalein as indicator. As the salt is formed it precipitates out since absolute alcohol dissolves salts only to a very small extent.

In the present case the preparation of the sodium salt was carried on as stated above. Early in the procedure many difficulties were met in that on titration of the alcoholic sodium hydroxide solution a strong odor was observed. This was the odor of acrylic acid. At the

same time the solution became slightly brown due to liberated iodine. Also a very small amount of salt would come down, this salt being slightly more soluble in absolute alcohol than most salts are. The precipitated salt was filtered off and washed with absolute alcohol. It was then partially dried by suction. The salt thus obtained was fairly white. However on standing for a few hours it would turn light brown while the odor of acrylic acid was very noticeable.

The filtrate which contained a fairly large amount of salt was divided into two portions. One was evaporated in vacuo over concentrated sulphuric acid, while the other was similarly treated by calcium chloride. The first turned brown before all of the alcohol had been driven off. The second kept fairly good, but when all of the alcohol had been removed it possessed a slight yellow color and the odor of acrylic acid. These two methods were used because evaporation of the alcohol over a flame or on the water bath serves only to break up the product, $CH_2ICH_2CO_2Na$, much faster than spontaneous evaporation in vacuo.

These experiments were continued varying the conditions slightly to see if decomposition could be prevented. The solution was kept cold during the titration and the precipitated salt being filtered off immediately, but the salt turned brown, in a few cases it turned very dark brown within an hour.

Analysis of Sodium Salt Prepared by Method I - Determinations for the amount of sodium in the salts thus obtained were carried on. The percentage of sodium in the samples examined was too high in every instance when the sample was calculated as $CH_2ICH_2CO_2Na$, but when calculated as $CH_2= CHCO_2Na$ it gave better results. In two instances it gave results very nearly equal to the theoretical for the latter.

Sample	Amount taken	Na_2SO_4	% Na
I	0.3050 gms.	.2295 gms.	24.363 %
II	0.2100 "	.1582 "	24.391 %
III	0.3500 "	.2640 "	24.394 %

Theoretical per cent Sodium in Sodium Acrylate = 24.462 %

A second scheme was to dissolve the sodium hydroxide in conductivity water, making a concentrated solution. A portion of this would be taken and titrated with the acid using phenolphthalein as indicator. The solution thus obtained was then evaporated in vacuo over concentrated sulphuric acid. In several instances the salt was nearly white. On standing a few hours it would turn brown. However I succeeded in getting a white salt which did not decompose. The sample when dried kept for three days.

All of the acid obtained had been used up in carrying out the experiments mentioned above. So new acid was required for the continuation of the work. This time I placed 100 grams glycerine in a 500 cc. round bottom flask and treated it according to the method mentioned in the preparation of glyceric acid. Another portion of 150 grams glycerine were placed in another flask and were treated the same way. After purification of the glyceric acid and it's separation from oxalic acid, it was further treated with phosphorous di-iodide to change it into $CH_2ICH_2CO_2H$.

Since two different glyceric acids were obtained these were kept apart and treated the same way with phosphorous di-iodide. The $CH_2ICH_2CO_2H$ thus obtained were also kept apart. A yield of 88 grams in the first case, and 66 in the second was obtained. These were recrystallized four times from ligroin until a white crystalline solid was

obtained in each case. During the last crystallization three different fractions were obtained in the case of the first acid, while two for the second acid. A series of melting points were taken. Results:

Fractions	I	II	III
Acid A	82.05	81.96	81.90
Acid B	82.00	81.92	

A quantitative determination of Iodine gave the following results:

Fractions	I	II	III
Acid A	63.429	63.421	63.428
Acid B	63.425	63.430	

Theoretical - 63.437 % iodine in β-iodopropionic acid.

Method II - This time a new scheme was tried for the preparation of the salt. The acid was dissolved in ether, while a concentrated solution of sodium hydroxide in absolute alcohol was prepared. The acid was then titrated with the sodium hydroxide solution using phenophthalein as the indicator. The salt precipitates almost white, and does not give odor of acrylic acid. It was washed with ether which had been treated with sodium hydroxide and metallic sodium.

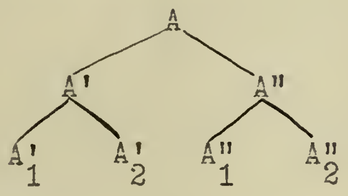
This sodium salt kept well without decomposing. It was analysed for sodium with results as follows:

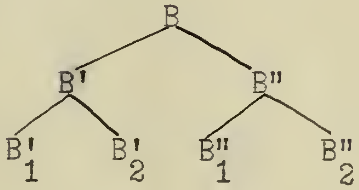
Sample	I	II	III
Wt. salt taken	.3000 gms.	.4000 gms.	.3505 gms.
Wt. Na_2SO_4 formed	.09600 " .	.1247 " .	.1122 " .
Wt. sodium in sample	.03108 " .	.04142 " .	.03628 " .
Per cent sodium in sample	10.360 %	10.354 %	10.352 %

Theoretical per cent sodium in sample = 10.363 %

Conductance of Salt and Acid -

Both salt and acid having been prepared in a sufficient degree of purity, the next step was the measurement of their conductances. I had two different acids and two salts corresponding to them. The following scheme was used in the measurement of the acids and the salts to eliminate personal errors. Let A and B equal the two different acids; A' and A" , B' and B' are checks run on acids A and B. One measurement is made at the highest concentration used. Then if A', A", B' and B" check, then A' and B" are dropped, but kept in case of emergency. The measurements at other concentrations is made from solutions A" and B'. This same scheme was used for the salt.





Preparation of Conductivity Water - The distilled water obtained in the laboratory is not good enough for measurement. It requires further purification. This is accomplished in the following manner. A special still for this purpose is used. It is filled with ordinary distilled water and to this is added a strongly alkaline solution of potassium permanganate. The water is then heated by steam coils until steam begins to issue at the delivery tube when further heating is stopped. The still and contents are allowed to stand over night. The next day the heating is resumed but half of the contents of the still are distilled over before collecting any water for the measurements. This is to remove the ammonia. When collecting the water care was taken to have it partially condensed only so that steam together with water was always issuing from the delivery pipe. This would prevent the absorption

of laboratory fumes.

The flasks, pipettes and other glass objects used in the measurements were carefully steamed for four to five days in order to remove any free alkali. Then they were washed with conductivity water, dried and weighed.

Measurement of the Acid - 200 cc. of a 0.02 N solution were prepared, solutions A_1, A_2, B_1, B_2 etc. corresponding to acids A_1, A_2, B_1, etc. The ionization conctant of the water used was 1.107×10^{-6}.

Measurement of β-Iodo-Propionic Acid

.02 N	R	K	Λ
A_1	125.96	.0004919	24.503
A_2	125.92	.00049093	24.504
B_1	125.96	.0004919	24.503
.01 N			
A_1	182.41	.0003386	33.857
A_2	182.47	.00033843	33.843
B_1	182.47	.00033843	33.843
.0075 N			
A_1	210.69	.00029297	39.062
A_2	210.69	.00029297	39.062
B_1	210.69	.00029297	39.062
.005 N			
A_1	262.71	.00023474	46.947
A_2	262.71	.00023474	46.947
B_1	262.71	.00023473	46.946
.0025 N			
A_1	380.75	.00016162	64.646
A_2	380.75	.00016162	64.646
B_1	380.70	.000161643	64.655
.001 N			
A_1	638.74	.000095893	95.893
A_2	638.74	.000095893	95.893
B_1	638.68	.000095903	95.903

R stands for the average of three readings taken for each of the solutions A_1, A_2, B_1, etc.

Measurement of Sodium Salt of β -Iodo-propionic Acid

.02 N	Resistance	K cor.	Λ
A	40.00	.00015467	77.336
B	40.00	.00015467	77.336
.01 N			
A	76.77	.0008048	80.480
B	76.72	.0008053	80.530
.0075 N			
A	101.11	.0006105	81.40
B	101.14	.0006103	81.37
.005 N			
A	149.60	.00041186	82.37
B	149.49	.00041214	82.43
.0025 N			
A	291.20	.00021047	84.19
B	290.14	.00021124	84.494
.001 N			
A	710.36	.000084922	84.92
B	709.70	.000085004	85.00

The resistance is the average of six readings.

Water correction used = .0000023

From the values obtained for the resistance of the solutions of the acid and salt at the different concentrations I obtained K cor. , Λ, $1/\Lambda$, and $(C\Lambda)^{n-1}$, where n = 2 in case of the acid and 1.45 in case of the salt. Then I plotted $1/\Lambda$ against $(C\Lambda)^{n-1}$ for both acid and salt to test the accuracy of the results. The points fell in a straight line as may be seen on plate number one.

Results for β -Iodo-propionic Acid :

Concentration	Λ	$1/\Lambda$	$(C\Lambda)^{n-1}$
.02 N	24.50	.04081	.4901
.02 N	24.50		
.01 N	33.86	.02954	.3385
.01 N	33.84		
.0075 N	39.06	.02560	.29296
.0075 N	39.06		
.005 N	46.95	.02130	.23473
.005 N	46.95		
.0025 N	64.65	.01547	.16163
.0025 N	64.66		
.001 N	95.90	.013128	.09590
.001 N	95.89		

The results for the sodium salt were as follows:

Concentration	Λ	$1/\Lambda$	$(C\Lambda)^{.45}$
.02 N	77.34	.01293	1.21700
.01 N	80.51	.012418	0.90070
.0075 N	81.39	.012290	0.80078
.0050 N	82.40	.012140	0.6710
.0025 N	84.34	.011835	0.4964
.0010 N	84.96	.011775	0.32972

The values when plotted gave $1/\Lambda_o$ = .011375 for zero concentration, or Λ_∞= 87.9 which may be taken as 88.

88. - 51.2 = 36.8 = $\Lambda_\infty CH_2ICH_2CO_2$

36.8 + 350 = 386.8 = $\Lambda_\infty CH_2ICH_2CO_2H$

From these values the ionization constant of the acid was found with results as follows:

Concentration	Λ	$\Lambda_\infty - \Lambda$.	K
.02 N	24.50	362.3	6.805×10^{-5}
.01 N	33.85	352.95	8.393×10^{-5}
.0075 N	39.06	347.74	8.713×10^{-5}
.0050 N	46.95	339.85	8.385×10^{-5}
.0025 N	64.65	322.15	8.386×10^{-5}
.001 N	94.90	201.80	7.976×10^{-5}

Average K = 8.371×10^{-5}

Preparation of Mono-iodoacetic Acid -

The measurement of the conductivity of this acid was performed by P. Walden (4) who prepared it from the action of iodine and iodic acid upon CH_3CO_2H. These measurements were repeated by J. H. Mitchell (7) of this laboratory during the summer of 1911. He prepared the acid in the same manner as Walden. My method of preparation was totally different from the above method. The object in view being to check Mitchell's work with an acid prepared in a different way than that used by Mitchell, in order to determine any constant error due to impurities, if present.

Preparation - The method used is that of Meyer and Jacobson (8) . In this method we start with monochlor-acetic acid. This is dissolved in water and treated with the required amount of potassium iodide at a temperature of 50°. The reaction is as follows:

$CH_2ClCO_2H + KI \rightleftharpoons CH_2ICO_2H + KCl.$

The potassium iodide is added in small portions at a time. On addition of potassium iodide the solution acquires a brown color due to the liberated iodine, but on stirring the solution it becomes a pale yellow color. This process is carried out until all of the potassium iodide has been added. The solution is then cooled and extracted with ether. On evaporation of the ether a slight brown colored iodo-acetic acid remains behind. The yield is good.

The acid thus obtained was further purified with low boiling ligroin 60 - 80°, following the same scheme used for the purification of β -iodopropionic acid. It was noticed that iodo acetic stays white from four to six days, but then it begins to acquire a light brown color which increases as the time increases. In this respect the beta acid is more stable than the alpha for the former stays white for a

longer time.

Preparation of Sodium Salt of Iodo-Acetic Acid -

No trouble was experienced in the preparation of the sodium salt of this acid. A concentrated solution of sodium hydroxide in absolute alcohol was prepared by dissolving sodium hydroxide in alcohol which had been distilled over sodium hydroxide, lime and metallic sodium in order to prepare very pure absolute alcohol. To this solution was then added the solid acid using phenolphthalein as indicator. Care was taken in adding a slight excess of the solid acid when the reaction was complete in order to be sure that there was no free alkali left. It was then extracted with absolute alcohol to remove free acid or alkali. After drying a quantitative test was made on both the acid and salt with results as follows:

Analysis of Acid.

	Sample I	Sample II
Amount acid taken	0.2560 gms.	0.3005 gms.
Amount AgI formed	0.3232 " .	0.3792 " .
Per cent Iodine in sample	68.242 %	68.224 %

Theoretical Amount of Iodine = 68.257 %

Analysis of Sodium Salt of Iodo Acid.

	Sample I	Sample II
Sample taken	0.5015 gms.	0.5240 gms.
Wt. Na_2SO_4 formed	0.1713 " .	0.1787 " .
Per cent Sodium in sample	11.050 %	11.04 %

Theoretical amount Sodium in sample = 11.061 %

The iodo-acetic acid being pure enough it was measured. The water was prepared as in the case of the beta acid. Water correction to be used = 0.0000021

Measurement of Iodo-acetic Acid.

.02 N	R (ohms).	Λ	Mitchell's Λ
A	46.55	66.445	66.59
B	46.59	66.39	
.01 N			
A	68.79	89.86	89.9
B	68.80	89.85	
.0075			
A	81.75	100.77	
B	81.80	100.71	
.005 N			
A	103.36	119.48	119.3
B	103.33	119.48	
.0025 N			
A	159.80	154.24	
B	159.80	154.24	
.001 N			
A	293.35	209.1	209.4
B	293.36	209.0	

R is the average resistance of solution, six readings being taken for each solution.

Measurement of Sodium Salt of Iodo-acetic Acid.

Concentration	Resistance	Λ	Mitchell's Λ
A .02 N	40.15	77.050	
B .02 N	40.17	77.014	76.91
A .01 N	77.29	79.954	80.02
B .01 N	77.28	79.965	
A .005 N	150.16	82.105	81.89
B .005 N	150.18	82.095	
A .001 N	710.84	85.06	84.91
B .001 N	710.80	85.066	

The resistance for each solution is taken as the average of six readings taken on each solution.

After both acid and salt had been measured the following factors were found: resistance of solution, K corrected, Λ, $1/\Lambda$, and $(C\Lambda)^{n-1}$, where n = 2 in case of the acid or 1.45 in case of the salt. Then I plotted $1/\Lambda$ against $(C\Lambda)^{n-1}$ for both acid and salt. The curves are shown in plate 2. From the curve for the sodium salt I found $1/\Lambda$. corresponding to 0 concentration. The value found was 88.5 . Since

$CH_2ICO_2H = \Lambda_\infty H^+ + \Lambda_\infty CH_2ICO_2^-$ and $\Lambda_\infty CH_2ICO_2Na = \Lambda_\infty CH_2ICO_2^- + \Lambda_\infty H^+$. Using the values 51.2 for $\Lambda_\infty Na^+$ and 350 for $\Lambda_\infty H^+$ I found $\Lambda_\infty CH_2ICO_2H$ to be 387.3. From these values the ionization of the acid K was found.

Values for Sodium Salt.

Concentration	$1/\Lambda$	$(C\Lambda)^{n-1}$	Λ
.02 N	.012978	1.2147	77.03
.01 N	.012507	0.9042	79.96
.005 N	.012180	0.6699	82.10
.001 N	.011760	0.3299	85.06

Table for the Acid.

.02 N	.01503	1.3283	66.42
.01 N	.01113	0.8985	89.86
.0075 N	.009927	0.75555	100.74
.0050 N	.008369	0.59740	119.48
.0025 N	.006484	0.38560	154.24
.001 N	.004782	0.20910	209.1

From the values for Λ and Λ_∞ for the acid I found the ionization constant for the acid K . The results are as follows:

Concentration	Λ	$\Lambda_\infty - \Lambda$	K
.02 N	66.82	320.48	7.195×10^{-4}
.01 N	89.85	297.45	7.008×10^{-4}
.0075 N	100.74	286.56	6.858×10^{-4}
.005 N	119.48	267.82	6.881×10^{-4}
.0025 N	233.06	233.06	6.590×10^{-4}
.001 N	178.20	178.20	6.335×10^{-4}

Conclusions.

I. The equivalent conductances at infinite dilution and 25° for the following substances are:

CH_2ICO_2Na = 88.5 (measured)

CH_2ICO_2H = 387.3 (calculated)

$CH_2ICH_2CO_2Na$ = 88. (measured)

CH I CH CO H = 386.8 (calculated)

II. The ionization constant of iodo-acetic acid at 25° is 6.98×10^{-5}.

III. The ionization constant of β-iodo-propionic acid at 25° is 8.37×10^{-5}.

IV. The α-iodine place influence ($I_{\alpha, I}$) at 25° from iodo-acetic acid is 0.5073

V. The β-iodine place influence ($I_{\beta, I}$) at 25° from β-iodo-propionic acid is 0.199

VI. The rule of thirds does not apply to iodine with an accuracy greater than 15% at 25° if the experimental data are correct, since $\frac{0.5073}{3} = 0.169$, while experimentally this value is 0.199

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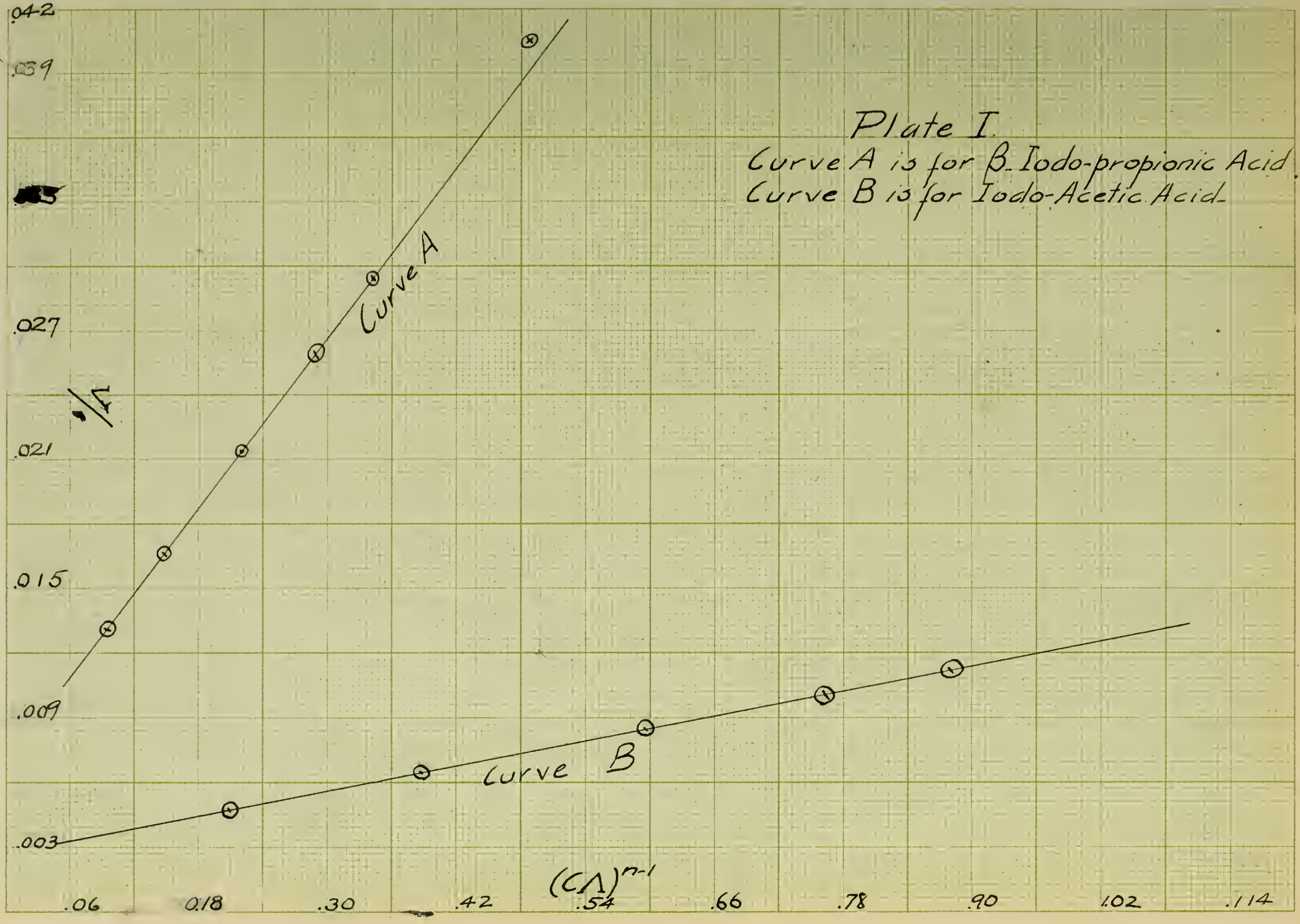

Plate I.

Curve A is for β-Iodo-propionic Acid.

Curve B is for Iodo-Acetic Acid.

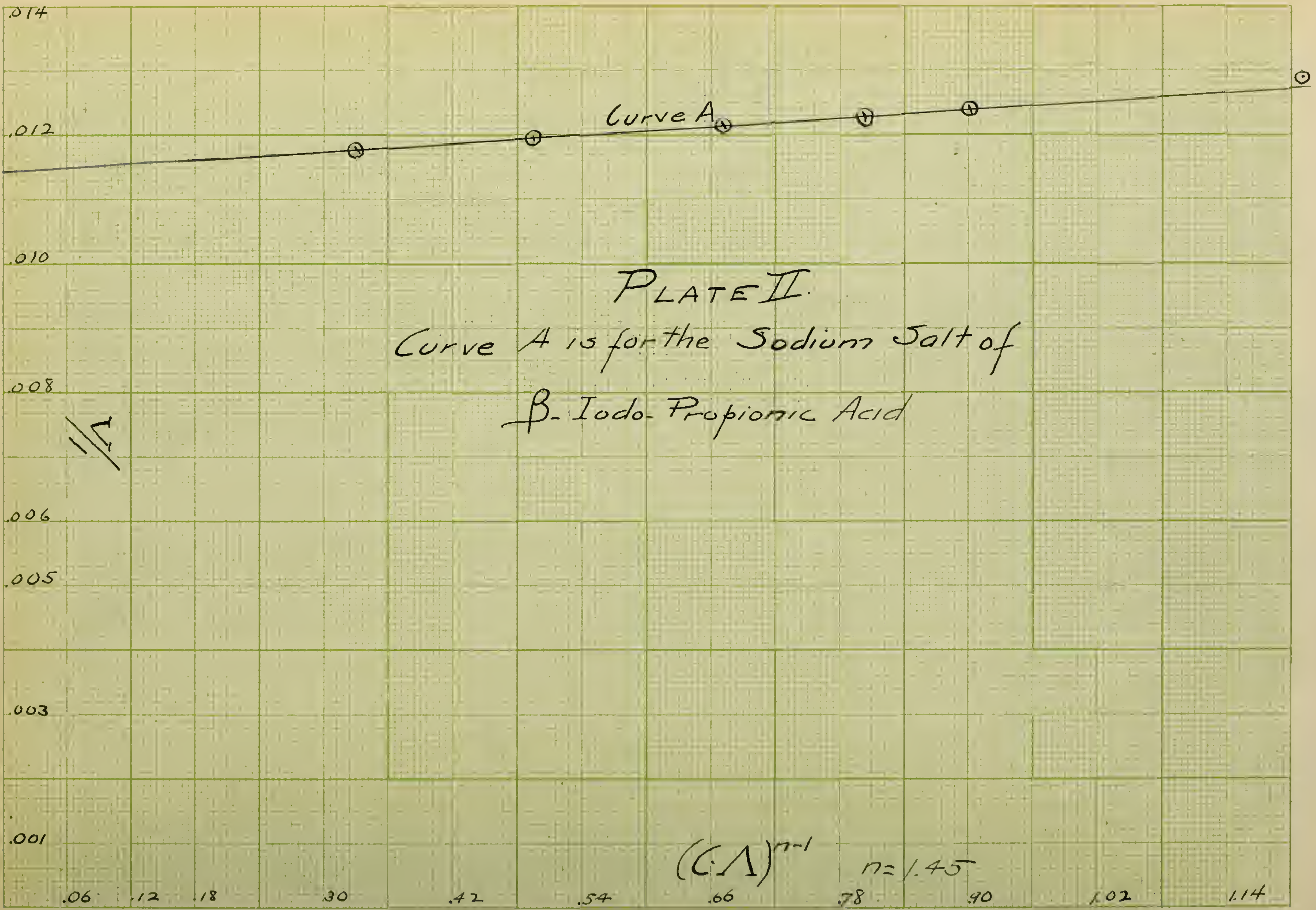

PLATE II.

Curve A is for the Sodium Salt of β-Iodo-Propionic Acid

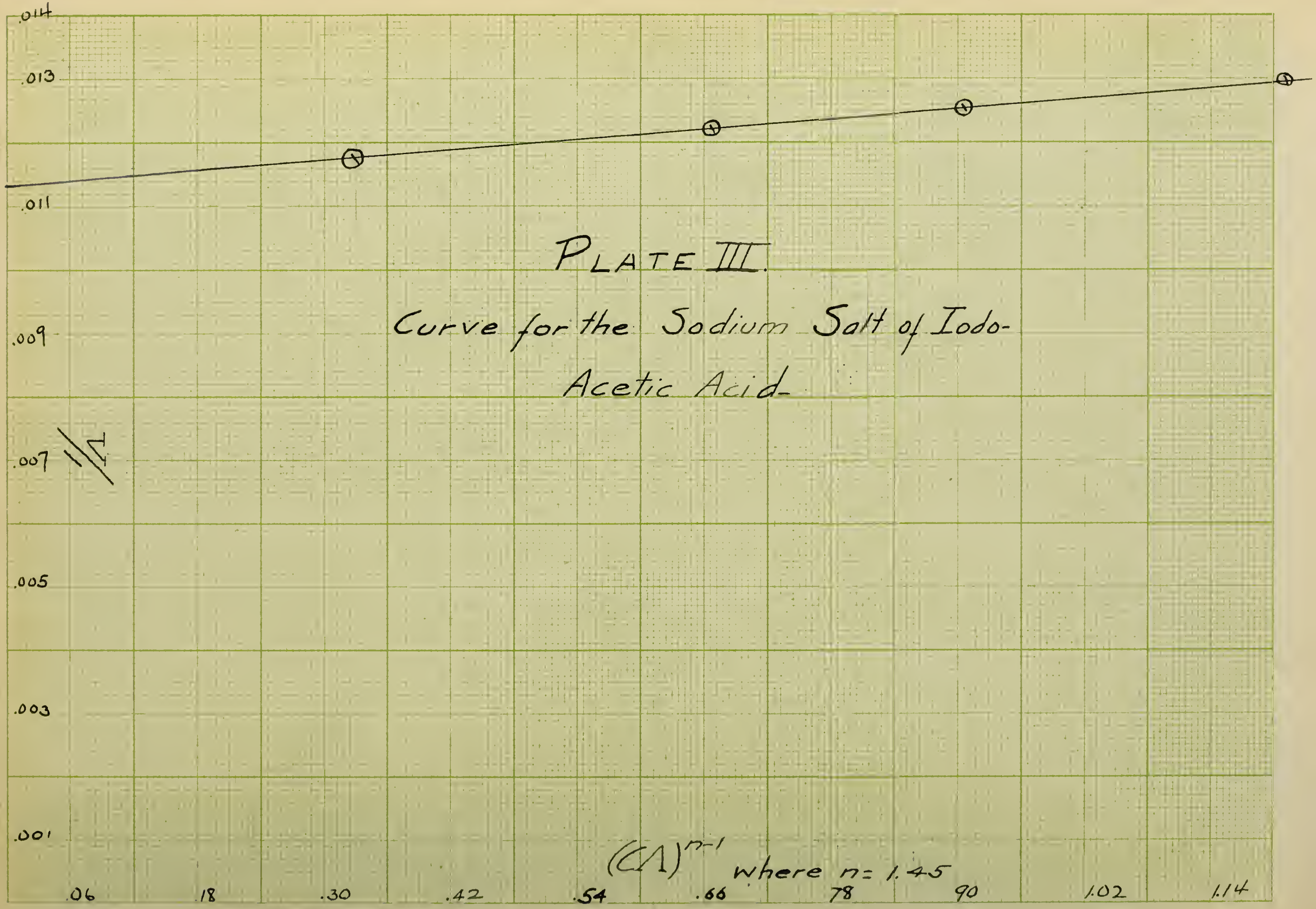

PLATE III.

Curve for the Sodium Salt of Iodo-Acetic Acid

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